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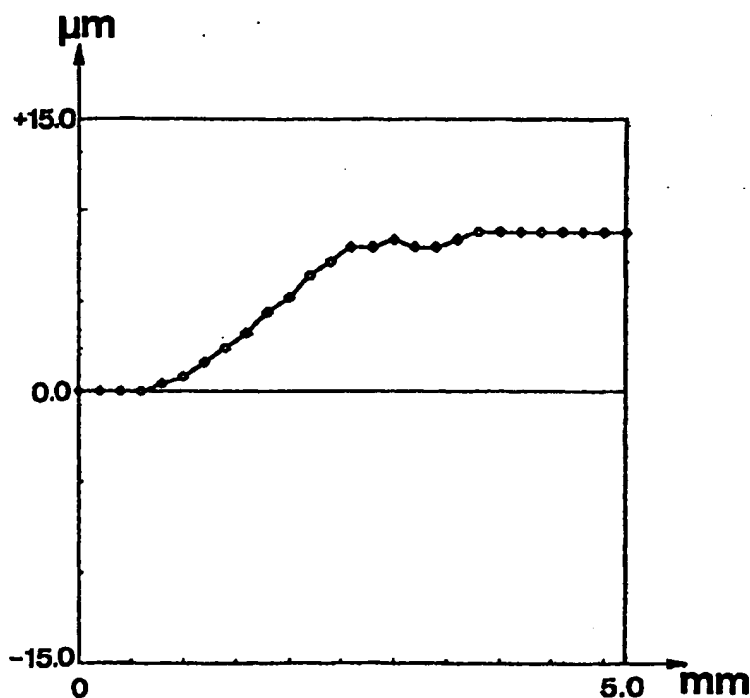
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(54) Title: PROCESS FOR PREPARING SILICA OR SILICA-BASED THICK VITREOUS FILMS ACCORDING TO THE SOL-GEL TECHNIQUE AND THICK FILMS THEREBY OBTAINED

(57) Abstract

It is described a sol-gel process allowing the preparation, on a substrate, of glassy films of silicon oxide or mixed oxides based on silicon oxide, of thickness above 1 micrometer, generally between 2 and 20 micrometers, and characterised by absence of defects, that turn out to be particularly suitable as waveguides in flat optical devices.



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"PROCESS FOR PREPARING SILICA OR SILICA-BASED THICK VITREOUS FILMS ACCORDING TO THE SOL-GEL TECHNIQUE AND THICK FILMS THEREBY OBTAINED"

Field Of The Invention

5 The present invention relates to a sol-gel process for the preparation of thick glassy films of silicon oxide or based on silicon oxide and to the thick films thus obtained.

 In the technology of solid state, with the term "film" is meant a thin layer of a material having a thickness generally comprised
10 between a few tens of nanometers (nm) and a few tens of micrometers (mm), said layer being supported over a substrate of another material, generally of flat geometry.

 The term "thick" typically refers to films of thickness larger than 1 μm .

15 Thick glassy films, deposited over a suitable substrate, are the object of extensive research in view of their foreseen use in the field of telecommunications, particularly telecommunications on optical and electro-optical cables.

 In the past, telephone communications and data transmissions
20 were realised transforming the signal into electronic impulses that were transmitted by means of cables of an electrically conductive material, generally copper.

 Nowadays, in particular for the long distances, transmissions on electrical cables have been almost completely replaced by
25 transmissions on optical fibers. As known, the optical fibers are glassy fibers whose structure comprises at least a central part, called nucleus, and an outer part, called mantle, made of glasses having slightly different chemical compositions; the different chemical composition gives rise to a difference in the refractive index of the
30 two materials that allows confining the optical signal in the nucleus.

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Commonly the mantle is made of pure silicon oxide, whilst the nucleus is made of a mixed oxide based on silicon oxide containing from a few percent to about 10% by mole of different oxides such as germanium oxide.

5 The optical fibers offer several advantages over electrical cables as means for information transmission, such as a lower level of noise and lower signal attenuation as well as a higher amount of information transmitted per unit time, resulting in a higher transmission rate.

10 Despite these advantages, it has not been possible so far to fully exploit the potentiality of optical communications: in fact, a complete communication system requires devices for processing signals, for instance for transforming voice into signal at the two ends of the cable in telephonic transmissions, or for amplifying the signal
15 along the fibre, that is rendered necessary due to unavoidable attenuation of the same signal. More generally, the so-called operation of signal commutation that is needed for delivering the same signal in the network requires suitable devices.

To this end, traditional electrical devices (electronic switches)
20 are presently used, and generally any operation on the signal requires a conversion into electrical signal followed by a possible further conversion back to optical signal. In these operations time and signal quality are lost. As a consequence, a strong need is felt for optical or electro-optical devices capable of guiding an optical
25 signal as well as of performing on it commuting operations comparable to those operated by electronic devices on electrical signals.

The main features that optical devices must have, are:

- material of very high transmittance, requiring absence of
30 inclusions and mechanical defects;

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- possibility of controlling through chemical composition the refractive index, that must be at least a few percent units higher than that of surrounding materials;

- flat geometry, for easy fit into automated production lines;

5 - thickness of a few μm , preferably between about 2 and 20 μm .

In order to ease integration of these devices into production and communication lines, the substrate should preferably be made of silicon or silicon oxide.

10 Background Of The Invention

Such devices are presently produced according to physical techniques, among which thermal oxidation of silicon, and those known as Sputtering, Chemical Vapor Deposition and Flame Hydrolysis can be cited. Another method consists in the vacuum
15 deposition on a silicon substrate of microparticles of silicon oxide obtained according to the Flame Hydrolysis technique.

However, these productions are complex, requiring costly working chambers and tools; some of these, such as silicon thermal oxidation, have a limit in the film thickness that can be obtained,
20 while others are exceedingly slow and are often characterised by low productivity and too high costs, so as not to allow an actual industrial exploitation of optical devices.

The most economically promising technology for massive production of glassy films on substrates is sol-gel. Under the name sol-gel are gathered different procedures for the preparation of oxides
25 of one or more elements in form of porous bodies, ceramics or glasses.

While differing from each other in the specific details, all sol-gel procedures share the following phases:

30 - preparation of a "sol", a solution or suspension in water,

alcohol or hydroalcoholic mixtures of forerunners of the elements whose oxide is to be prepared. Generally used as forerunners are the alkoxides, of formula $M(OR)_n$, where M represents the element whose oxide is desired, the group -OR is the alkoxide moiety, and n represents the valence of element M; soluble salts of the element M, such as chlorides, nitrates and exceptionally oxides, may be used in place of alkoxides. During this phase the forerunners begin to hydrolyse, that is, alkoxide moieties or other anions bonded to element M are replaced by -OH groups;

10 - sol gelation, requiring from a few seconds up to some days, depending on chemical composition and temperature of the solution; during this phase hydrolysis of the possibly remaining forerunner is completed and condensation occurs, consisting in the reaction of -OH groups belonging to different molecules with
15 formation of one free water molecule and an oxygen bridge between atoms M, M' (alike or different), according to the reaction:



The product obtained in this phase is called alcogel, hydrogel depending on the cases, or more generally "gel" as widely used in
20 the English literature.

 - gel drying; in this phase the solvent is removed by simple evaporation or through hypercritical transformation into gas inside an autoclave; there is obtained an extremely porous dry body, that may have an apparent density ranging from about 10% to about
25 50% of the theoretical density of the oxide of that composition;

 - dry gel densification by thermal treating at a temperature generally comprised between 800 °C and 1200 °C depending on the gel chemical composition and on the parameters of the previous process phases; in this phase the porous gel densifies
30 obtaining a glassy or ceramic compact oxide of theoretical density,

with a linear shrinkage of about 50%.

If gelation phase is not too fast, it is possible to lay a liquid film of sol on a substrate, eventually resulting in a oxide supported film. Obtaining a oxide film on a substrate in this way is however easily
5 feasible only for a thickness up to some tenths of micrometer. Up to such values of thickness, cohesive forces in the film are weak, and forces adhering the film on the substrate prevail, so that during the densification phase there is not in-plane shrinkage of the film and densification only involves its thickness decrease. At values of
10 thickness above one micrometer, on the other hand, inner cohesive forces of the film become prevailing and during densification in-plane shrinking of the film takes place as well: the result is film fragmentation into "islands" spread over the substrate surface and poor adhesion of the film to the substrate.

15 This thickness of about 1 μm represents a technological limit for sol-gel technique, as indicated for instance in "SOL-GEL science: the physics and chemistry of SOL-GEL processing", Brinker and Scherer, Academic Press, 1990, a comprehensive review of the knowledge in the field. As already stated above, films prepared in this way are
20 defined thin or thick when they have a thickness below or above about 1 μm , respectively.

For the production of thick films through the sol-gel technique it has been proposed to prepare a sol containing, in addition to normal forerunners, a dense material in the form of nanospheres,
25 that is, spheres of dimensions of about 10 nm. This approach is exposed in the paper "SOL-GEL derived thick coatings and their thermomechanical and optical properties", Menning et al., SPIE Vol. 1758, SOL-GEL Optics II (1992), pages 125-134. This technique however can hardly be implemented practically; besides, despite
30 the fact that the first papers on the technique were published more

then five years ago, actual feasibility of thick films by this route has not been proven yet.

Another proposed approach is to prepare thick films through repeated depositions of thin films; any single layer must be densified before deposition of the subsequent layer. An example of this kind of procedure is given in "Deposition of thick silica-titania SOL-GEL films on Si substrates" Symms et al., Journal of Non-Crystalline Solids, 170 (1994), pages 223-233. According to the literature, by this way it is possible to prepare multilayer thick films. On the other hand, as stated in the cited paper, in order to obtain films of good mechanical and optical characteristics any single layer must have a thickness not higher than about 0.25 μm , so that the production of a film of thickness about 10 μm requires about 40 deposition and densification steps.

Thus, the production of large amounts of flat waveguides by the sol-gel route is still an open problem.

It is thus an object of the present invention to provide a sol-gel process for the preparation of thick glassy films of silicon oxide or based on silicon oxide, as well as to provide glassy supported films of thickness higher than 1 μm , preferably between 2 and 20 μm .

Disclosure Of The Invention

According to the present invention, these objects are obtained with a sol-gel process for the preparation of thick glassy films of silicon oxide or based on silicon oxide, comprising the following phases:

- preparation of a sol comprising at least one soluble forerunner of at least one element chosen among Si, Ge, C, Sn, Pb, P, As, Sb, B, Al, Ga, Bi, Ti, Zr, S and Hf, where the molar ratio between the soluble silicon forerunner and any other soluble forerunner is at least 1:1, said sol containing at least 10 moles of H_2O per each mole of said at

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least one soluble forerunner and an acid capable of causing hydrolysis of said at least one soluble forerunner, said acid having a concentration comprised between 0.03 and 0.5 N;

- complete hydrolysis of said soluble forerunners;
- 5 - addition to the sol from about 0.7 to about 3.0 mols of SiO₂ per mole of said at least one soluble forerunner;
- formation of a sol film on a substrate;
- gelation of the sol through solvent evaporation;
- densification of the gel film thus obtained through thermal
- 10 treatment.

Brief Description Of Drawings

The invention will be described in detail with reference to the accompanying drawings, in which:

- Figure 1 shows the result of a profilometric test on a sample of
- 15 the invention before the densification operation, showing sample thickness variations along a line that crosses the film edge;
- Figure 2 shows the result of a profilometric test on the same sample of Figure 1 after densification;
- Figure 3 is a schematic view of a sample of the invention,
- 20 obtained according to the interferometric technique in order to put in evidence possible defects of substrate-film interface;
- Figure 4 shows another image of the same sample and with the same view of Figure 3, with the only difference that the image in Figure 4 has been obtained according to the "dark field" technique,
- 25 as explained below.

Modes For Carrying Out The Invention

- In the first phase of the process according to the invention it is prepared an extremely diluted sol of a silicon alkoxide or of a mixture of alkoxides corresponding to the desired glassy
- 30 composition. In mixed oxides, the molar ratio between silicon oxide

and oxides of other elements may be 1:1 or higher in the case of germanium, while it is generally not lower than 5:1 when elements such as titanium, aluminium or boron are employed.

This sol is preferably of very low concentration and is obtained
5 using at least 10 mols of H₂O per mole of alkoxides, preferably from about 20 to about 100 mols of H₂O per mole of alkoxides and more preferably from about 30 to about 40 mols of H₂O per mole of alkoxides. Preferred alkoxides are those where the alcoholic moiety comes from methyl or ethyl alcohol, as these alkoxides are easily
10 hydrolysed and the resulting alcohols may be easily removed by evaporation. Taking silicon as an example, silicon alkoxides may also be defined as silicic acid ortho-esters, and are known in the field as TMOS, that's the acronym for Tetra-methyl-ortho-silicate, Si(OCH₃)₄, and TEOS, the acronym for Tetra-ethyl-ortho-silicate, Si(OCH₂CH₃)₄.
15 H₂O is added as a solution of an acid of concentration such as to yield a pH value comprised between 0.3 and 1.5. The preferred acid is HCl: in this case the acid concentration is comprised between 0.03 and 0.5 N and preferably between 0.04 and 0.2 N.

Alkoxides hydrolysis is an equilibrium reaction; as the invention
20 process necessarily requires that hydrolysis at this stage be completed, and that no traces of alcohol remain in the subsequent phases, hydrolysis is pushed to its stoichiometric completion by distilling the forming alcohol. Distillation is generally performed under pumping, keeping the pressure in the hydrolysis container at a level
25 below 10 mbar, and preferably comprised between 3 and 5 mbar. This phase may be accelerated and favoured by operating at a temperature comprised between 30 and 40 °C. Hydrolysis is stopped when the volume of alcohol recovered in a suitable flask is about 110% of the volume of alcohol stoichiometrically produced by
30 alkoxides hydrolysis; recovering an over-stoichiometric volume one

takes into account the amount of water that may evaporate along with alcohol as an azeotropic mixture, thus ensuring total alcohol removal.

To the thus obtained sol there are added from about 0.7 to 3
5 mols of SiO_2 , preferably about 2 mols of SiO_2 per each starting silicon alkoxide mole. In the preferred embodiment of the invention, SiO_2 compound is in the form of extremely fine powders, such as the compound obtained by flame hydrolysis. SiO_2 by flame hydrolysis is a particular form of extremely pure powdery silica, with particles of
10 granulometry of about 10 nm, and it is produced feeding SiCl_4 to an oxyhydrogen flame. This product is commonly available on the market and may be obtained for instance by Degussa under the tradename Aerosil OX-50. Homogeneous dispersion of flame hydrolysis SiO_2 into the sol may be favoured by mechanical or
15 ultrasonic stirring.

The thus obtained sol is deposited on a substrate according to known techniques, e.g. by means of dip-coating or spin-coating, the first one consisting in dipping in and extracting from the sol, at a constant pre-set speed, the substrate kept in vertical position, and
20 the second one in pouring a pre-set amount of sol on the substrate while spinning this latter, at a speed generally comprised between 500 and 5000 rpm.

The sol films thus obtained on the substrate are preferably caused to gel suddenly through quick solvent evaporation. Gelation
25 consists in the condensation of $-\text{OH}$ groups bonded to different atoms of silicon or of other possibly present elements, according to reaction (I) given above. Oxygen bridges between two atoms of metal, silicon or germanium are formed, eventually resulting in the formation of an oxidic gel.

30 Instantaneous gelation is obtained in the simplest way by

sudden heating of the film from room temperature at a temperature of about 300-400 °C, for instance introducing the substrate with the film into a pre-heated oven. The film may then be left in the oven for a few minutes, to enhance its mechanical strength. Once extracted
5 from the oven, the film is stable and can be left exposed to air indefinitely. This film is constituted by a dry gel, having the same chemical composition of the final oxide, but with a porous structure.

The last process phase consists in densification of the film, that is realised in subsequent thermal treatment steps.

10 As known in the field, the dry porous gel obtained is generally subjected, as a first preparation step of the densification procedure, to a thermal treatment in oxidising atmosphere, for instance between 300 °C and 1000 °C, preferably between 500 °C and 800 °C in air or oxygen, in order to remove through combustion the
15 remaining traces of organic compounds, alcohol or alcoholic moieties, that can have been left in the gel pores.

A subsequent step consists in a film dehydration or purification treatment, in order to remove the -OH groups possibly remaining in the film after gelation, solvent evaporation and combustion removal
20 of organic moieties. In a first embodiment of the process of the invention this is obtained by flowing in the gel pores a gaseous dry dehydrating agent, such as HCl possibly diluted in an inert gas. Alternatively, the same procedure is realised by using HCl diluted in H₂ in the inert gas.

25 Once the pre-set temperature in the above said range is reached, substrate and film are kept at such a temperature for a given time, generally comprised between 10 minutes and 1 hour in the presence of a dehydrating atmosphere.

Before realising the final densification phase, substrate and film
30 are heated at a temperature comprised between 400 °C and 1000

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°C, preferably between 500 °C and 800 °C, in a flowing inert gas, such as 99.99% pure helium, to wash the film.

The densification phase then involves heating substrate and sample in a flowing inert gas. Specifically, substrate and film are brought to temperatures comprised between 1200 °C and 1400 °C in a 99.99% pure helium during a time preferably comprised between about 10 and about 30 minutes.

This process is fully compatible with silicon oxide substrates. When the substrate is made of silicon, using HCl mixtures in helium may give rise to microerosions, known in the field as "pittings", on the same substrate surface. To avoid this, it is possible to resort to mixtures where the inert gas contains hydrogen along with HCl, with an acid/hydrogen ratio that varies depending on the treatment temperature, according to the conditions indicated in a paper of G. A. Lang, published on RCA Review of 1963, Vol. 24, page 448. This paper shows that the volume percent of HCl that may be present admixed with hydrogen without giving rise to pitting becomes higher the higher the temperature: as an example, pitting may be avoided with mixtures containing a HCl volume up to about 1.5% of the volume of hydrogen working at about 1200 °C; up to about 3% at about 1240 °C; and up to about 5% at about 1270 °C.

Objectives and advantages of the present invention will be better appreciated by the experts in the field by reading the following examples, that are meant to illustrate the invention but by no means are to be considered as limiting its scope. In the Examples from 1 to 5, the preparation and check of a silicon oxide film on a substrate according to the invention is shown, while in Example 6 it is shown the preparation of a film by using a starting sol of different composition.

EXAMPLE 1: Preparation of a porous film on a substrate

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50 grams of TEOS are added to 150 cc of HCl solution 0.1 N in a flask. The thus obtained solution is made homogeneous subjecting it to simultaneous mechanical and ultrasonic stirring during about 10 minutes. A clear monophasic solution is obtained. The solution is heated at 40 °C; after 1-2 minutes, extraction of ethyl alcohol formed by TEOS hydrolysis is begun, maintaining the sol at a temperature of 20 °C in the flask connected, through a Rotavapor, to a pump that brings the pressure in the reaction flask to about 5 mbar. The condensing pipe of the Rotavapor is kept at a temperature of about -20 °C to ensure complete condensation of the formed alcohol. The pump is disconnected from the system when in the collecting flask there are measured about 56 cc of liquid, essentially consisting of ethyl alcohol. 28.8 grams of Aerosil OX-50 Degussa are added to the thus obtained sol, and the mixture is made homogeneous by ultrasonic stirring during 10 minutes. By using the thus obtained sol, some films are prepared through the dip-coating technique, dipping and extracting from the sol a silicon substrate at a speed of 0.5 cm per second. The sol film is instantaneously gelled placing it into an oven preheated at 400 °C and keeping it in the oven for about 10 minutes. On this film, not yet densified, a profilometric test is carried out by using a Rodenstock RM 600 profilometer. This technique allows performance of non-destructive tests to investigate a surface profile; tests may either be performed along one single line, obtaining the surface heights variations along the chosen line, or scanning the surface along parallel lines, thus obtaining the surface heights variations of the whole surface. In the present example a single-line mode profilometric test has been performed. The result is shown in Fig. 1, reporting film thickness in micron on the vertical axis and displacement in millimeters on the film plane on the horizontal axis.

The horizontal axis zero value corresponds to the border of the zone reached by the sol during dipping of the substrate in the same sol. The resulting film thickness, apart from the edge zone, is of about 10 μm .

5 EXAMPLE 2: Porous film densification

The sample prepared as given in Example 1 is cleaned from traces of possibly remaining organic compounds and densified according to the following thermal treatment:

- heating from room temperature to 800 °C in helium at an
10 heating rate of 4 °C per minute;
- treatment in a 10% anhydrous HCl – 90% helium mixture during half an hour at 800 °C;
- heating in helium up to 1370 °C at an heating rate of 4 °C per minute;
- 15 - rapid cooling, taking about 6 hours, down to room temperature.

A profilometric tests similar to the one previously described is carried out on the thus densified film. The test result is represented in Fig. 2, similar to Fig. 1, and shows a film thickness of about 8 μm .

20 EXAMPLE 3: Substrate and film check

The dense film sample obtained in Example 2 is inspected with an interferometric microscope (Zeiss, Mod. AXIOVERT). The results are shown in Fig. 3: focussing the microscope at the interface between the perfectly transparent film and the silicon substrate, black spots
25 corresponding to silicon surface defects are noted. The image in Fig. 3 shows a line, L, representing the edge of film F on substrate S: the silicon oxide film lays on the upper part of the image.

EXAMPLE 4: Film check

The same sample of Example 3 is now inspected in "dark field",
30 using the same view direction and the same Zeiss AXIOVERT

microscope. The "dark field" technique consists in lighting the sample with light directed towards the centre of the viewing field and with an incidence degree on the sample of about 45°. In these conditions, if sample surface has no defects, light is not reflected in the observation direction and the sample looks black; vice versa, if the sample has defects, these diffuse light in any directions, comprising the observation direction, so that the appearance of shining spots or areas in the microscope field reveals a non-perfectly planar surface. The results of this inspection are shown in Fig. 4. It can thus be noted that defects are present on the substrate S alone, while film F, corresponding to a zone with no bright spots or zones, results completely free of defects.

EXAMPLE 5: Thick films production with no substrate defects generation

A sample obtained according to the procedure of Example 1 is densified according to the following thermal treatment:

- heating from room temperature to 800 °C in oxygen at an heating rate of 4 °C a minute;
- treating at 800 °C with a gaseous mixture containing one mole of HCl per 100 mols of H₂ per 2500 mols of inert gas, such as N₂ or He;
- heating in helium up to 1370 °C at an heating rate of 4 °C a minute.

By inspecting the thus obtained sample with the microscope, according to both the "clear field" and "dark field" techniques, no defects are detected.

COMPARATIVE EXAMPLE 6

The procedures of Examples 1 and 2 are repeated, with the only difference that the HCl concentration for preparing the starting sol is lowered at 0.01 N. The result is a broken film showing poor adhesion onto the substrate.

The analysis of tests results shows that the process of the invention allows the obtainment of thick supported films. In particular, Fig. 2 shows that by the invention process a film about 8 μm thick has been obtained having side dimensions of several millimeters. Figures 3 and 4 show that, although the substrate surface presents a few point defects (black spots in Fig. 3) the oxidic film formed according to the invention process has an upper surface with no defects (lack of bright spots in the upper part of the image in Fig. 4, corresponding to the zone where the film is). In this image, defects at the film-substrate interface, that is, under the film, are no longer visible, because in the "dark field" technique this interface is no longer lighted up being shielded by the mirror plane represented by the intact film. Silicon surface defects are avoided if, in the last part of the densification process, a HCl-hydrogen mixture in inert gas instead of HCl alone in inert gas is used, as explained in the cited paper of G. A. Lang and as shown in Example 5. Films obtained according to the process of the invention are hence endowed with good optical surfaces, allowing their use in optics.

Finally, despite the fact that the sol-gel technique has been known and investigated for a number of years, and despite the fact that the single steps of the present process of the invention may have previously described in the specialised literature, only the process of the invention, characterised by the sum of its steps as a whole, allows the obtainment of the above exposed results, that could not be obtained before by the experts in the sol-gel field.

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CLAIMS

1. Process according to the sol-gel technique for the preparation of thick glassy films of silicon oxide or based on silicon oxide, comprising the following phases:
 - 5 - preparation of a sol comprising at least one soluble forerunner of at least one element chosen among Si, Ge, C, Sn, Pb, P, As, Sb, B, Al, Ga, Bi, Ti, Zr, S and Hf, where the molar ratio between the soluble silicon forerunner and any other soluble forerunner is at least 1:1, and the sol contains at least 10 mols of H₂O per each mole of said at
10 least one soluble forerunner and an acid capable of causing hydrolysis of said at least one soluble forerunner, said acid having a concentration comprised between 0.03 and 0.5 N;
 - complete hydrolysis of said soluble forerunners;
 - addition to the sol of from about 0.7 to about 3.0 mols of SiO₂
15 per mole of said at least one soluble forerunner;
 - formation of a sol film on a substrate;
 - gelation of the sol through solvent evaporation;
 - densification of the gel film thus obtained through thermal treatment.
 - 20 2. Process according to claim 1, characterised in that in said sol preparation phase there are used from 30 to 40 mols of H₂O per each mole of said at least one soluble forerunner.
 3. Process according to claim 1, characterised in that in said sol preparation phase it is used a mixture of soluble forerunners of
25 silicon and germanium such that the mole ratio between silicon and germanium is equal to or higher than 1:1.
 4. Process according to claim 1, characterised in that in said sol preparation phase it is used a mixture of soluble forerunners of
30 silicon and of one or more elements chosen among titanium, aluminium and boron, such that the mole ratio between silicon and

the mixture of the other elements is higher than 5:1.

5. Process according to any of the preceding claims, characterised in that said soluble forerunners are alkoxides of said elements.

5 6. Process according to any of the preceding claims, characterised in that in said sol preparation phase there are employed Tetramethylorthosilicate, $\text{Si}(\text{OCH}_3)_4$, or Tetraethylorthosilicate, $\text{Si}(\text{OCH}_2\text{CH}_3)_4$ as silicon alkoxides.

10 7. Process according to claim 1, characterised in that in said sol preparation phase H_2O is added in the form of a solution of an acid having such concentration as to produce a pH value comprised between 0.5 and 1.5.

8. Process according to claim 7, wherein H_2O is added as a solution of HCl of concentration comprised between 0.03 and 0.5 N.

15 9. Process according to claim 8, wherein H_2O is added as a solution of HCl of concentration comprised between 0.04 and 0.2 N.

10. Process according to claim 1, characterised in that said soluble forerunners hydrolysis phase is caused to happen in a hydrolysis container and performed up to stoichiometric completion by distillation of the alcohol formed in the hydrolysis, keeping the
20 pressure in said hydrolysis container at a value below 10 mbar.

11. Process according to claim 10, wherein pressure in said hydrolysis container is comprised between 3 and 5 mbar.

12. Process according to claim 10 or 11, wherein the
25 temperature in said hydrolysis container is kept at a value comprised between 30 °C and 40 °C.

13. Process according to claim 1, characterised in that said soluble forerunners hydrolysis phase is continued until the distilled volume is about 110% of the theoretic volume of alcohol formed in
30 the same hydrolysis.

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14. Process according to claim 1, characterised in that said film gelation phase is realised by introducing the substrate with the sol film in an oven preheated at a temperature comprised between about 300 °C to about 400 °C.

5 15. Process according to claim 1, characterised in that said film densification phase comprises, in turn, the following phases:

- thermal treatment between about 500 °C and 800 °C in an oxidising atmosphere in order to remove through combustion possible traces of organic compounds, alcohol or alcoholic moieties
10 present in the gel;

- film dehydration or purification through thermal treatment at a temperature comprised between 500 °C and 800 °C and maintaining film and substrate at said temperature for a time comprised between about 10 minutes and 1 hour in a flow of a
15 gaseous mixture comprising up to 10% of HCl in an inert gas;

- heating of the film on the substrate at a temperature comprised between 500 °C and 800 °C in a pure inert gas flow to realise film washing; and

- film and substrate heating at a temperature comprised
20 between about 1200 °C and 1400 °C in an inert gas flow.

16. Process according to claim 15, characterised in that in said dehydration phase a mixture of HCl diluted in H₂ in said inert gas is used.

17. Process according to either claim 15 or 16 wherein, when
25 the substrate is made of silicon, said gaseous mixture of HCl in an inert gas further contains hydrogen with a molar ratio 1:100 between HCl and hydrogen.

18. Process according to claim 16, wherein the inert gas is 99.99% pure helium.

30 19. Supported thick glassy films of silicon oxide or based on

- 19 -

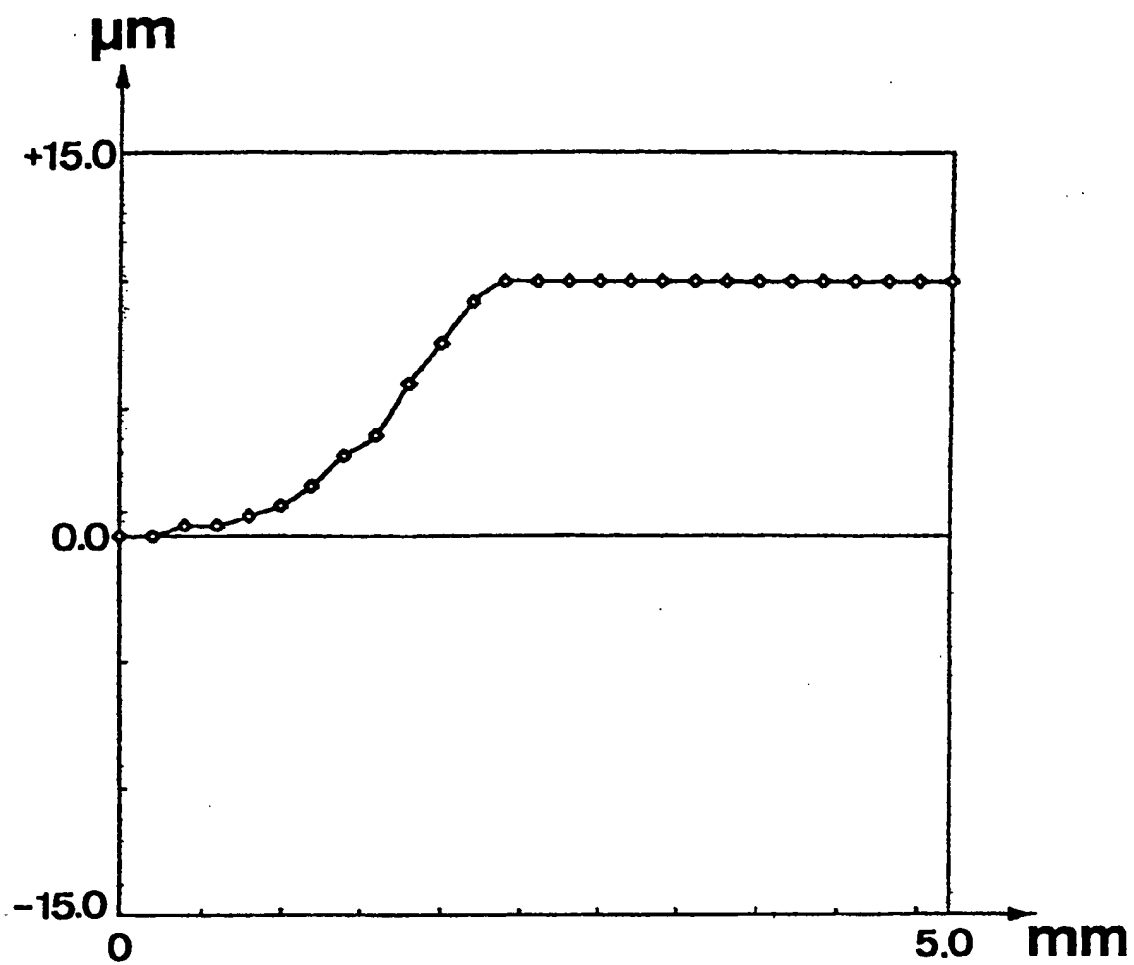
silicon oxide obtained according to the process of any of claims from 1 to 18.

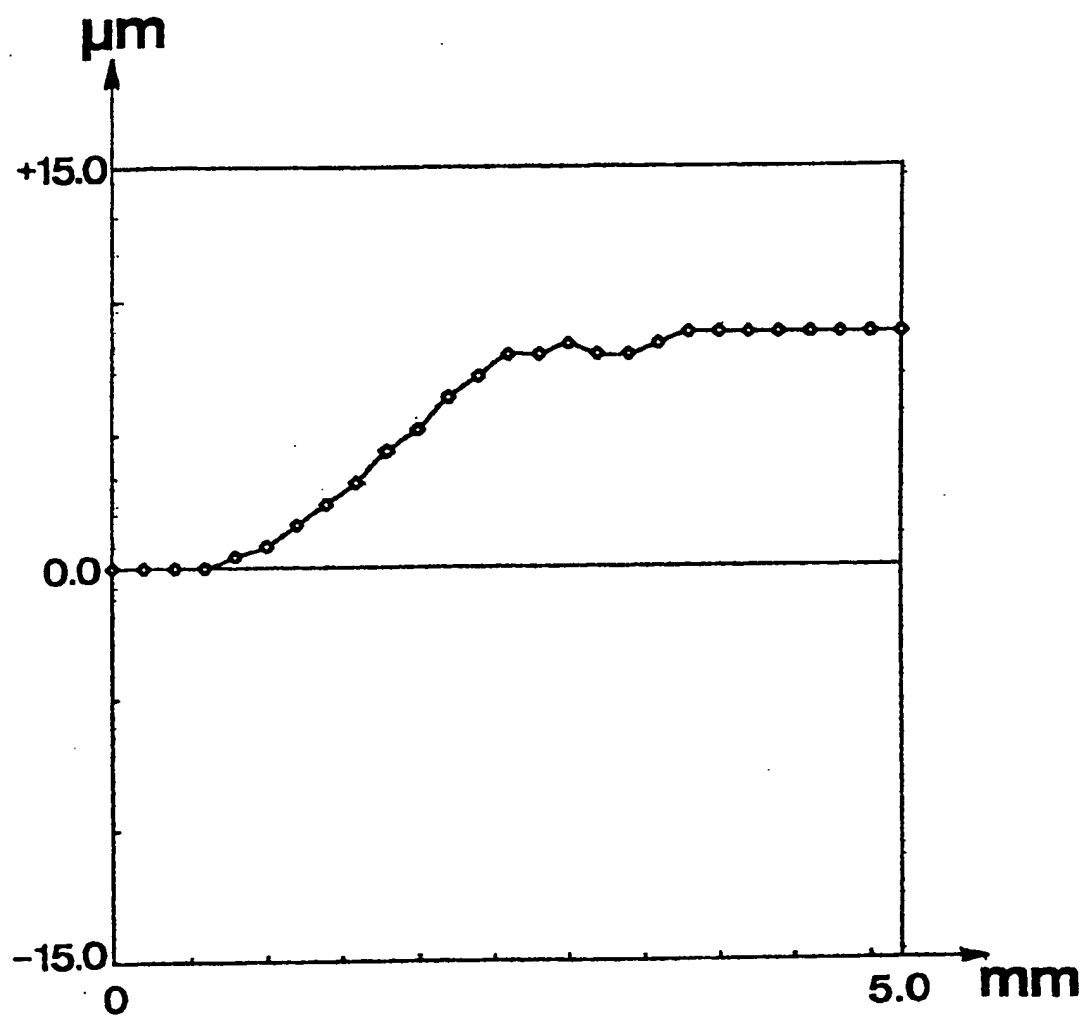
20. Sol composition for the preparation according to the sol-gel technique of thick glassy films of silicon oxide or based on silicon oxide, characterised by comprising:

- at least one soluble forerunner of at least one element chosen among Si, Ge, C, Sn, Pb, P, As, Sb, B, Al, Ga, Bi, Ti, Zr, S and Hf, where the molar ratio between the soluble silicon forerunner and any other soluble forerunner is at least 1:1;
- 10 - at least 10 mols of H₂O per each mole of said at least one soluble forerunner; and
- an acid capable of causing hydrolysis of said at least one soluble forerunner, said acid having a concentration comprised between 0.03 and 0.5 N.

15 21. Sol composition for the preparation according to the sol-gel technique of thick glassy films of silicon oxide or based on silicon oxide, characterised by comprising:

- at least one soluble forerunner of at least one element chosen among Si, Ge, C, Sn, Pb, P, As, Sb, B, Al, Ga, Bi, Ti, Zr, S and Hf, where
- 20 the molar ratio between the soluble silicon forerunner and any other soluble forerunner is at least 1:1;
- at least 10 mols of H₂O per each mole of said soluble forerunner;
- an acid capable of causing hydrolysis of said at least one
- 25 soluble forerunner, said acid having a concentration comprised between 0.03 and 0.5 N;
- from about 0.7 to about 3.0 mols of SiO₂ per each mole of said at least one forerunner;
- and in that at least one soluble forerunner is hydrolysed.

**Fig. 1**

**Fig. 2**

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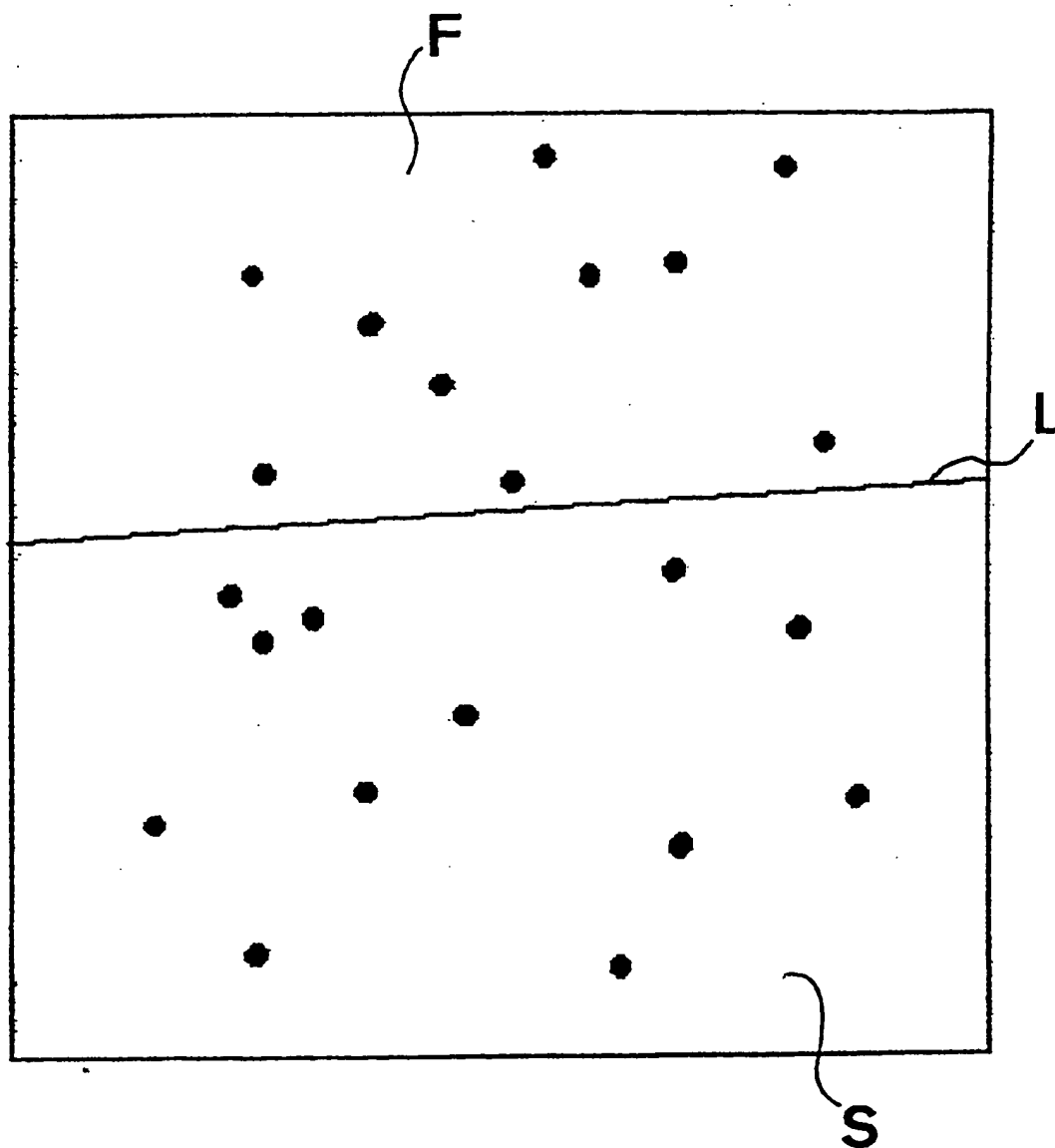


Fig. 3

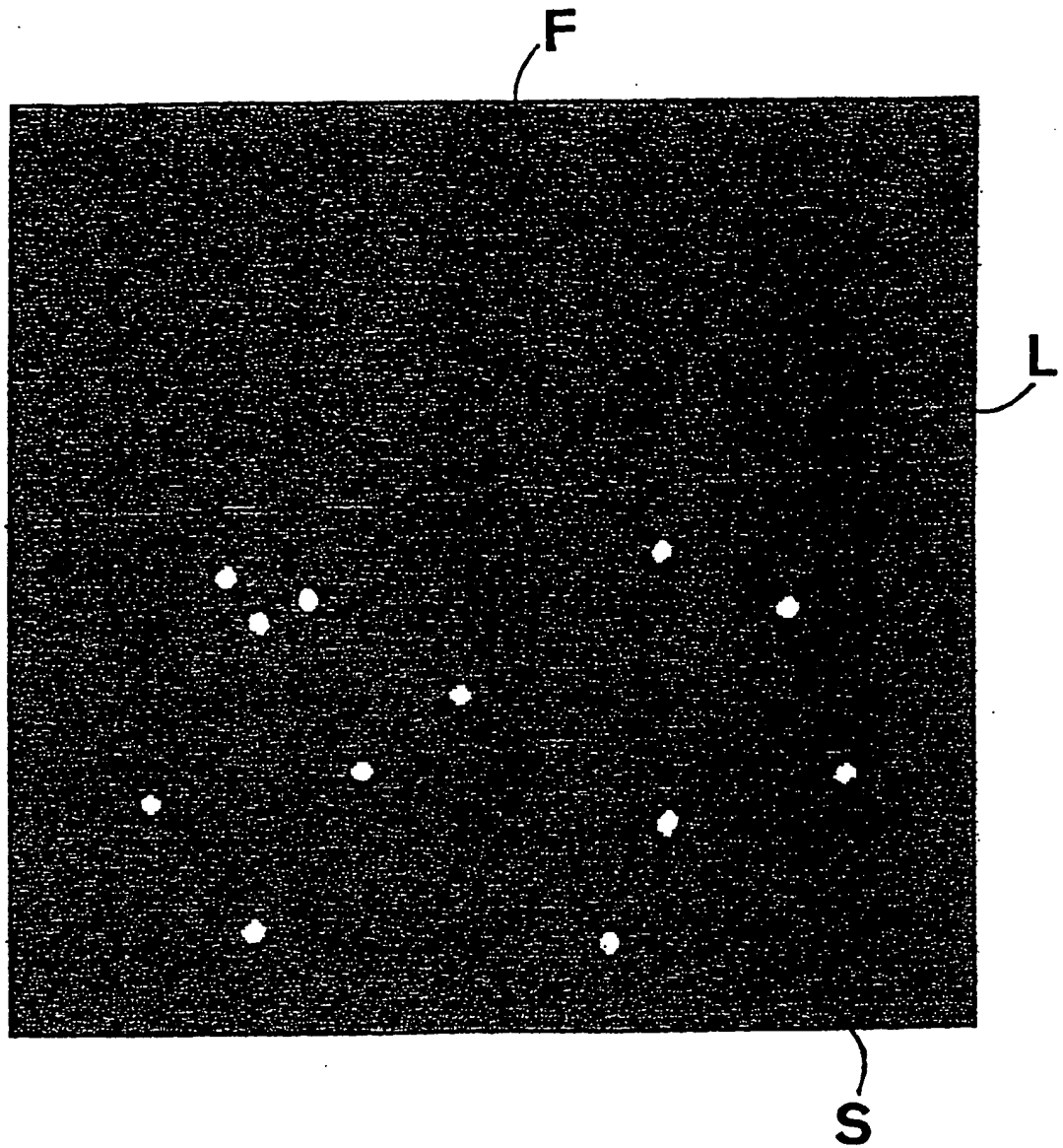


Fig. 4

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/IT 99/00284

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C01B33/12 C23C18/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|--|-----------------------|
| A | MENNING ET AL : "Sol-Gel derived thick coatings and their thermomechanical and optical properties" SPIE, vol. 1758 Sol-Gel Optics II, 1992, pages 125-134, XP000864342 cited in the application page 126, line 1 - line 37 | 1 |
| A | WO 96 29447 A (UNIV KINGSTON) 26 September 1996 (1996-09-26) page 6, line 28 -page 7, line 7 --- -/-- | 1 |

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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Date of the actual completion of the international search

26 January 2000

Date of mailing of the international search report

15/02/2000

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Authorized officer

Clement, J-P

INTERNATIONAL SEARCH REPORT

International Application No
PCT/IT 99/00284

| C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT | | |
|--|--|-----------------------|
| Category | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
| A | <p>DATABASE WPI Section Ch, Week 199317 Derwent Publications Ltd., London, GB; Class L03, AN 1993-140188 XP002128370 & JP 05 078103 A (RICOH KK), 30 March 1993 (1993-03-30) abstract</p> <p style="text-align: center;">---</p> | 1 |
| A | <p>PATENT ABSTRACTS OF JAPAN vol. 016, no. 249 (C-0948), 8 June 1992 (1992-06-08) & JP 04 055328 A (SUMITOMO ELECTRIC IND LTD), 24 February 1992 (1992-02-24) abstract</p> <p style="text-align: center;">-----</p> | 1 |

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/IT 99/00284

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
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| | | JP 11502262 T | 23-02-1999 |
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| JP 04055328 A | 24-02-1992 | NONE | |